

# Functionalized Aligned Carbon Nanotubes as a Novel Catalytic Electrode for PEM Fuel Cells

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## 1 Introduction

The future of the hydrogen-based economy depends, to a great extent, on successful commercialization of low-cost, high-efficiency devices that convert various forms of energy via H<sub>2</sub> to electricity. The proton exchange membrane fuel cell (PEMFC) is one such device. A PEMFC generates electric power at a relatively low temperature with hydrogen as the fuel and oxygen (air) as the oxidant. At the core of a PEMFC is the membrane-electrode assembly (MEA) which consists of a polymer electrolyte layer sandwiched between an anode and cathode. At the surface of the anode electrocatalyst, hydrogen is oxidized through the reaction



The protons are subsequently transported to the cathode side and react with the electrocatalytically reduced oxygen to form water:

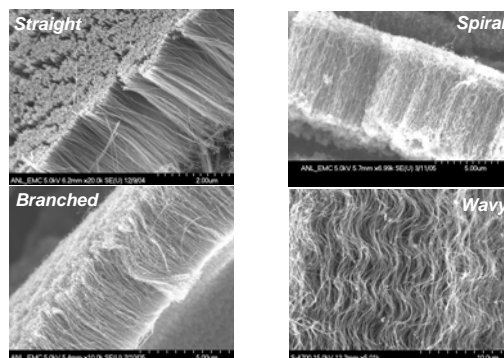


Reaction (2) is also known as the oxygen reduction reaction (ORR). Both reactions (1) and (2) need to be promoted by electrocatalysts. At present, the most effective electrocatalyst is made of platinum metal supported on amorphous carbon. The Pt loading on the cathode side is typically four times higher than that of anode due to the sluggishness of the ORR. Since platinum is a precious metal with limited natural reserves, its usage adds a significant cost to a PEMFC vehicle. For a 60-kW midsize fuel cell vehicle (FCV), the platinum cost alone is over \$2400 based on current Pt loading and market price [1]. This is prohibitively expensive if the FCV is to be viable in a commercial market.

Replacing Pt catalyst with a low-cost alternative is an extremely challenging proposition. Among various materials currently being pursued, transition metal based N<sub>4</sub>-macromolecules appear promising. For example, Dodelet and coworkers demonstrated ORR catalytic activity from macromolecules containing iron coordinated by four pyrrolic rings such as phthalocyanine and porphyrin, both in the original and pyrolyzed forms [2]. They also found that similar activity can be achieved by treating iron acetate with ammonia at elevated temperature [3]. They attributed the ORR activity to an active site with a phenanthroline type structure where the transition metal (TM) ion was coordinated to two pyridinic nitrogens, -TMN<sub>2</sub>-. A major concern for these materials is their stability in the acidic and oxidative environments such as those found in the PEMFC cathode. Since the catalyst was prepared by calcining the impregnated organometallics over amorphous carbon, gradual activity losses through the corrosion of the catalyst as well as the support could be an issue [4].

At Argonne National Laboratory, we are exploring a novel approach of preparing Pt-free electrocatalysts based on our recent effort in synthesizing aligned carbon nanotubes (ACNT) through a chemical vapor deposition (CVD) process. In our preliminary experiment, we successfully prepared uniform, dense layers of multi-wall carbon nanotubes on a polished substrate surface under carefully controlled conditions. The nanotube diameter can be varied from 10 to 100 nm with the orientation perpendicular to the substrate. The geometry and shape of the nanotube depends on the CVD conditions and the precursor. A few examples of ACNT bundles are shown in Figure 1. The CVD mixture is composed of an inexpensive, volatile TM organometallic compound such as Fe or Co metallocene, a hydrocarbon, and the carrier gas of H<sub>2</sub>/Ar. At elevated temperatures, the organometallics decomposes to form a catalytic center on the substrate that catalyzes the hydrocarbon into a graphene sheet, which subsequently folds into a nanotube.

Simultaneous decomposition of organometallics and hydrocarbons leads to a continual evolution of the nanotube with the transition metal atomically embedded throughout the graphene layer. By adding ammonia to the carrier gas, we found that the ORR activity of the ACNT was significantly enhanced as measured by cyclic voltammetry in an oxygen-saturated perchloric acid electrolyte. There are several advantages of using functionalized ACNT as the electrode catalyst. First, ACNT has a graphitic structure that is more chemically inert than amorphous carbon. Our electrode catalyst has a higher resistance to acid etching and oxidative corrosion. Gas-phase mixing in CVD results in better distribution and dispersion of the TM throughout the ACNT than the impregnation/calcination approach. The ACNT-based electrode also brings in some novel aspects that could revolutionize future fuel cell design. Since the nanotubes are vertically aligned, this alignment can be transferred onto the polymer electrolyte membrane to form a spatially oriented electrode assembly [5]. Furthermore, the ACNT layer can be patterned into various 3-dimensional shapes, mimicking the flow field of PEMFC bipolar plates. Such membrane electrode assemblies will have improved electrical conductivity, better fuel gas/air distribution, and enhanced catalyst utilization. This paper describes our recent effort in synthesis of ACNT with N-doping to improve the electrocatalytic activity, as well as investigation of the nature of the catalytic center using synchrotron x-ray absorption spectroscopic methods.



**Figure 1. Aligned carbon nanotube bundles with different geometric shapes**

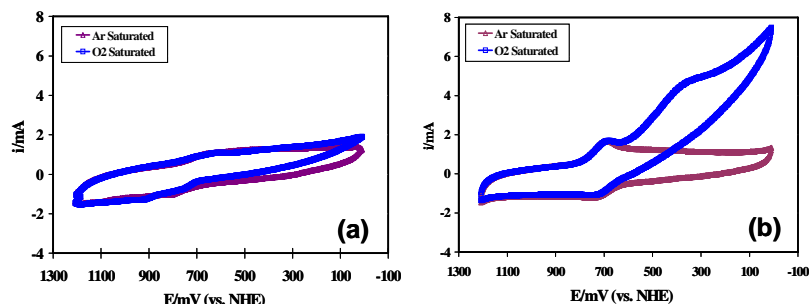
## 2 Experimental

ACNTs were prepared in a tubular CVD reactor inside a two-temperature-zone furnace. The liquid mixture of ferrocene (Sigma-Aldrich) and xylene (Sigma-Aldrich) was injected and vaporized in the low-temperature zone and the ACNTs were formed over polished quartz plates positioned in the high-temperature zone. The carrier gases used in the CVD process contained a mixture of  $H_2$  and Ar. For the N-doping study, ammonia was also added to the gas mixture. The images of ACNT were taken by a high-resolution scanning electron microscope at Argonne's Electron Microscopy Center. The cyclic voltammograms (CVs) for the ORR over ACNT electrodes were measured in oxygen-saturated perchloric acid electrolyte using Ag/AgCl as the reference electrode. *In situ* x-ray absorption spectroscopic investigation (EXAFS and XANES) of the Fe active site under different polarization potentials was performed at Beamline 13BM of the Advanced Photon Source at Argonne National Laboratory.

## 3 Results and Discussion

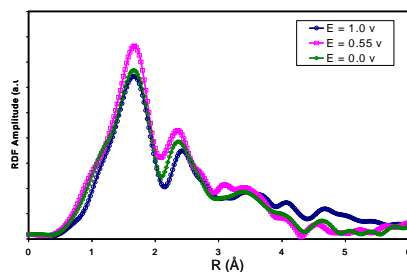
**Impact of N-doping on ORR activity:** Our study indicated that adding ammonia leads to N-doping into the ACNTs, most likely in the form of pyridinic nitrogen. Such functional groups, when they are adjacent to each other, can coordinate with Fe to form the  $-FeN_2-$  moiety, which is catalytically active toward ORR, according to the previous study [3,5]. Figure 2 shows the cyclic voltammograms of two ACNT samples prepared without (a) and with (b) nitrogen doping. Two measurements were performed for each sample with the acidic electrolyte purged with argon or saturated with oxygen. The difference between the measurements reflects the electrocatalytic activity towards oxygen reduction. As shown by Figure 2, both the onset potential and the current

are significantly higher for N-doped ACNT sample. This observation is consistent with our hypothesis of iron coordinated with pyridinic nitrogen as the active site.



**Figure 2.** CVs of two ACNT samples prepared through a CVD process in which ammonia was absent (a) or present (b) in the input mixture.

**Nature of Catalytic Active Site:** In our previous report, we identified the functional group  $-\text{FeN}_2-$  as the active site for oxygen reduction through a static state x-ray absorption spectroscopy (XAS) investigation on ACNT. We have since conducted *in situ* XAS experiments in which the ACNT was used as the working electrode in an electrochemical cell subjected to different polarization potentials. Figure 3 shows the radial distribution functions (RDF) obtained through Fourier transformation of EXAFS data taken at the Fe K-edge when the ACNT was under three different polarization potentials,  $E = 1.0$  V,  $0.55$  V and  $0.0$  V (vs. NHE). RDF generally provides the coordination shell structure surrounding the metal being selectively probed. Our XANES results indicate that iron in the ACNT is mainly in the  $\text{Fe}^{+3}$  state at  $E = 1.0$  V. However, when the potential was decreased to  $0.55$  V, which is below the ORR onset potential, iron was reduced to  $\text{Fe}^{+2}$ . The first shell coordination number counter-intuitively increased at this potential; based on general knowledge, a lower oxidation state should lead to lower O ligation. This is, however, consistent with the hypothesis that oxygen can only be activated by  $\text{Fe}^{+2}$ , as is observed in biological systems. Activated  $\text{O}_2$  binds with  $\text{Fe}^{+2}$ , which leads to an increase of the coordination number. Further decreasing the polarization potential to zero volts greatly enhanced the turnover frequency of oxygen reduction and reduced the transient lifetime of activated  $\text{O}_2$ , leading to lower first shell coordination.



**Figure 3.** Radial distribution function of Fe obtained at different polarization potentials

#### 4 Conclusions

Aligned carbon nanotubes with electrocatalytic activity for ORR were successfully synthesized using a CVD method with N-doping. *In situ* XAS suggested that  $\text{Fe}^{+2}$  is the active site in activating oxygen during ORR. This is consistent with the voltammetric behavior of this catalyst, which shows the onset for ORR coinciding with the reduction peak for  $\text{Fe}^{3+}$ .

## References

1. E. J. Carlson, "Direct Hydrogen PEMFC Manufacturing Cost Estimation for Automotive Applications," DOE Hydrogen Program Annual Merit Review, May 16-19, 2006
2. M. Lefèvre, J. P. Dodelet, and P. Bertrand, *J. Phys. Chem. B*, **2005**, 109, 16718
3. M. Lefèvre, J. P. Dodelet, and P. Bertrand, "Molecular Oxygen Reduction in PEM Fuel Cells: Evidence for the Simultaneous Presence of Two Active Sites in Fe-Based Catalysts," *J. Phys. Chem. B* **2002**, 106, 8705-8713
4. H. A. Gasteiger, S. S. Kocha, B. Sompalli, and F. T. Wagner, *Applied Catalysis B: Environmental*, **56** (2005) 9-35
5. D.-J. Liu and J. Yang, "Method of fabricating electrode catalyst layers with directionally oriented carbon support for proton exchange membrane fuel cells," *U.S. Patent Application*
6. J. Yang, D.-J. Liu and X. Wang, "A Novel Electrode Catalyst for Proton Exchange Membrane Fuel Cell using Aligned Carbon Nanotube," *Fuel Cell Seminar 2005 Extended Abstract*

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